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Chlorine Free Technology for Solar-Grade Silicon Manufacturing

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D.S. Strebkov, A. Pinov, V.V. Zadde, E.N. Lebedev, E.P. Belov, N.K. Efimov, and S.I. Kleshevnikova
INTERSOLAR Center, Moscow, Russia

K. Touryan and D. Bleak
National Renewable Energy Laboratory

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CHLORINE FREE TECHNOLOGY FOR SOLAR-GRADE SILICON MANUFACTURING

Strebkov D.S., Pinov A., Zadde V.V., Lebedev E.N., Belov E.P., Efimov N.K., Kleshevnikova S.I.,. INTERSOLARCenter, 2, 1-st Veshnaykovsky proezd, 109456, Moscow, Russia. Tel. (+7095) 171-19-20, fax: (+7095) 170-51-01, E-mail: viesh@dol.ru

K.Touryan, D. Bleak

National Renewable Energy Laboratory (NREL), 1617 Cole Boulevard Golden, Colorado 80401-3393, USA

Due to development of solar energy industry the significant increase of polysilicon feedstock (PSF) production will be required in nearest future[1,2]. That's why creation of special technology of solar grade polysilicon feedstock production is important problem. Today, semiconductor-grade polysilicon is mainly manufactured using the trichlorosilane ($SiHCl_3$) distillation and reduction. The feed-stock for trichlorosilane is metallurgical-grade silicon, the product of reduction of natural quartzite (silica). This polysilicon production method is characterised by high energy consumption and large amounts of wastes, containing environmentally harmful chlorine based compounds.

In the former USSR the principles of industrial method for production of monosilane and polycrystalline silicon by thermal decomposition of monosilane were founded. The process consists of two stages [3]:

1) Etherification of trichlorosilane for further producing of triethoxysilane proceeding in accordance with the reaction:

$$SiHCl_3 + 3\,C_2H_5OH \xrightarrow{catalyst} SiH(OC_2H_5)_3 + 3\,HCl$$

2) Catalytic disproportion of triethoxysilane proceeding in accordance with the reaction:

$$4\,SiH(OC_2H_5)_3 \xrightarrow{catalyst} SiH_4 + 3\,Si(OC_2H_5)_4$$

This technology was proved in industrial scale at production of gaseous monosilane and PSF.

We offered new chlorine free technology (CFT). Originality and novelty of the process were confirmed by Russian and US patent [4,5]. This technology differs by the following:

1. The reaction of metallurgical-grade silicon with ethanol at the 280 °C in the presence of a catalyst:

$$Si + 3\,C_2H_5OH \xrightarrow{catalyst} Si(OC_2H_5)_3H + H_2$$

2. The catalyst enchanted disproportion (i. e. simultaneous oxidation and reduction) of triethoxysilane will lead to the production of monosilane and tetraethoxysilane:

$$4\,Si(OC_2H_5)_3H \xrightarrow{catalyst} SiH_4 + 3\,Si(OC_2H_5)_4$$

3. Dry ethanol and secondary products such as high purity SiO_2 or silica sol can be extracted by hydrolysis of tetraethoxysilane. Ethanol will be returned to Stage 1:

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4\,C_2H_5OH$$

4. Monosilane purification from admixtures is implemented using less energy demanding methods of condensation and sorption. Silicon proceeding decomposed pyrolytically to pure silicon and hydrogen:

$$SiH_4 \xrightarrow{850° \div 900°C} Si + 2\,H_2$$

Due to absence of chlorine and chlorinated compounds and unrealizable wastes the process is ecologically safe. The originality of the CFT is that removing of tetraalcoxysilane from technological cycle doesn't lead to negative consequences or for technology, or for ecology. This is most important feature of the CFT, which allows to covert tetraethoxysilane into valuable product like stable dispersion of Si dioxide in water – silicasol. By isolation of tetraethoxysilane during hydrolysis, return of ethyl alcohol to direct synthesis of ethoxysilanes and high conversion rate of metallurgical silicon into goods products –PSF, high purity monosilane and silicasol – are ensured. CFT provides a substantial reduction of energy consumption (40 kWh per one kg of polysilicon vs. 250 kWh required for one kg of PSF produced by conventional trichlorosilane method) According to pre-calculations; cost of polysilicon feedstock for large-scale production is not more than 15 USD per 1 kg [6].

During the period from 2000 till 2003 the scientific and design works on creation of theoretical and experimental basis for chlorine free alcoxysilane technology of solar and electronic grade PSF production implemented has been in cooperation and with financial support of NREL. The following works were executed during the period:

- Investigations of the process of triethoxysilane production by interaction of metal silicon and ethanol were executed; effective solvent, catalyst and optimal regimes of the process were selected; design of the reactor was also elaborated.
- Thermodynamic calculations for possible reaction of tetraethoxysilane hydration were executed. The following reactions are of the most interest:

1. $Si(OC_2H_5)_4 + H_2\uparrow \rightarrow SiH(OC_2H_5)_3 + C_2H_5OH$

2. $3Si(OC_2H_5)_4 + Si + 4H^{\cdot} \rightarrow 4SiH(OC_2H_5)_3$

3. $3Si(OC_2H_5)_4 + Si + 2H_2\uparrow \rightarrow 4SiH(OC_2H_5)_3$

It was found out that these reactions are thermodynamically allowed.

- Investigations on tetraethoxysilane hydration by calcium hydride (CaH_2) were implemented. It was determined that the reaction occurs with high conversion tetraethoxysilane to silane level (more than 95%)
- New construction of monosilane pyrolysis apparatus was designed.
- Scheme of tetraethoxysilane hydrolysis stage and returning of ethanol into the process was developed.
- Technological schemes of the pilot plant complex for PSF production were elaborated.

During 2003 year, the design documentation for pilot plants complex for solar grade PSF production using chlorine-free technology with capacity 400 kg per year was created (Phase 2). This work was executed basing on results of previous Phase 1, as well as technical solutions found during the design process.

The aim of creation of the pilot plan complex is as following:

- finalizing of separate stages and processes of PSF production
- measuring of main parameters of the process for specifying of discharge rates for raw materials, by-products and energy consumption
- finalizing of hardware implementation of the process stages for further design of bigger capacity apparatus.
- accumulation and testing of test samples of PSF aiming determining of its quality and appropriateness for use in different industries (electronics, solar energy products)
- specification of cost of the products (PSF, triethoxysilane, high purity monosilane, silicasol)
- elaboration of initial data for industrial scale design.

The elaboration of design documentation was implemented according to the Work breakdown structure approved by NREL (table 1).

The design works were executed as follows:

1. Preparation and agreement of initial data for design works.
2. Technological schemes for separate pilot installations with determination of material flows and technological regimes, as well as elaboration of technical requirements for design of control and measurement equipment, for electrical equipment and for non-standard equipment etc.

3. Elaboration of correspondent parts of design documentation: control and measurement equipment, technical projects of non-standard equipment, specifications, layout, solutions for the equipment placing, documentation, selection of electrical equipment etc.

Table 1. Work breakdown structure for phase 2.

1. Elaboration of technological documentation for design
1.1. Raw monosilane production through disproportionation of triethoxysilane
1.2. Production of triethoxysilane through direct interaction of metallurgical silicon with ethanol
1.3. Producing of PSF by monosilane pyrolysis (including energy supply)
1.4. Producing of silica sol through hydrolysis of tetraethoxysilane
1.5. Deep purifying of raw monosilane

The project is elaborated according to existing in Russia technological, constructing and sanitary standards; it foresees arrangements ensuring constructional reliability, fire and explosion safety, population protection and sustainable operation in emergency conditions, as well as environment protection measures

Characteristics of main raw materials for CTF presented in table 2. As main raw materials the metallurgical silicon is used with comparatively low purity and ethanol, which at the stage of silica-sol production is returning to the process.

Table 2.

Name	Main parameters
Metallurgical silicon grounded	Mass share of silicon, % - not less than 98,0 Fraction content,% - bigger than 0,5 mm – not more than 5,0 not more than 0,5 – 0,072 mm – not less than 75,0 smaller than 0,072 mm – not more than – 25,0
Ethyl alcohol dehydrated, technological	Mass share of alcohol, % - not less than 98,8 Water content, % - not more than 0,1

Primary goal of any process of PSF production is ensuring of conditions at which the content of micro admixtures in PSF is minimum, because this determines its suitability for manufacturing of electronic products.

The most important role thus plays micro admixtures of electro active elements, namely elements of III and IV groups of Periodic system (acceptors and donors), which in many respects determine electro physical characteristics of silicon and operational characteristics of electronic devices. Special importance has acceptor admixture of boron since at subsequent PSF processing into monocrystal silicon by floating-zone method and by Chohralski method, the concentration of boron admixture remains constant, in contrast to other elements. The residual level of the boron content determines quality of the production.

In the CTF the removal of boron in technological process occurs at two stages:

1. at purifying of raw triethoxysilane due to linkage of boron in solid nonvolatile complexes;

2. at catalytical disproportionation of triethoxysilane; because of the reaction selectivity the boron and some other elements (phosphorus,arsenic etc.) do not form volatile gaseous hydrides (B_2H_6, PH_3, AsH_3 etc.), and their liquid compounds are removed with liquid tetraethoxysilane.

Thank to this the produced PSF has unique electro physical characteristics: specific resistance on boron is higher than 10000 Ω·cm, and on donors - higher than 600 Ω·cm.

Measures on excluding possibilities of pollution of intermediate and main products during the technological process were undertaken at designing of the CTF. It is achieved by the appropriate choice of constructional materials for the equipment, pipelines, armature, use of minimum quantity of nipples connections, selection of optimum conditions of welding.

The big attention in the project is given to creation of original apparatuses ensuring maximal output of main products. Especially it concerns to the reactor for direct synthesis of raw triethoxysilane in which optimum contact of reacting components: technical silicon, dehydrated ethanol and catalyst – is provided.

Reactor of disproportionate of triethoxysilane it is implemented in such a manner that mixing of input components occurs due to educed gaseous monosilane and does not demand mechanical mixing devices. Thanks to this necessary tightness of the reactor and absence of pollution of gaseous monosilane with impurities from environmental atmosphere is provided. Thus, high conversion of triethoxysilane into monosilane (up to 95 %) in disproportionate reactor is provided. Similar conditions are ensured in the rest non-standard equipment of the CTF.

One of the basic advantages the CTF is ecological safety of production process [7]. First of all, it is ensured by the absence in the technological cycle of aggressive and harmful products such as chlorine, chorus hydrogen and other chlorine-containing products. Moreover, ecological safety of manufacture is ensured by absence of waste gaseous emissions, as well as liquid and solid waste products.

Main products (table 3) for the new method of PSF production are:

- Monosilane and monosilane mixtures with other gases.
- Electronic grade feedstock silicon.
- PSF for PV industry.

The technological process allows changing assortment and shares of the products in total amount depending on market situation.

High quality of monosilane and SGPF are confirmed by measurements. The admixtures presence is at the level of sensitivity of modern instruments. Specific resistance of monocrystalline silicon samples produced by float zone technique is more than 10 000 Ώ.cm, and lifetime of minority carriers is up to 1000 μs.

At the same time there is 24 kg of tetraethoxysilane per 1 kg of monosilane in the yield. To convert it to other useful materials several technologies were elaborated:

- As result of hydrolysis of tetraethoxysilane, silica sols are produced; they can be used as coupling agent at manufacturing transfer-molds, for textile and construction materials strengthening, for creation of composite and other new materials. After thermal treating of silica sols SiO_2 is obtained; it can be used for manufacturing of optical glass fiber and quartz wares,
- Through organ magnesium synthesis of tetraethoxysilane wide used silicone polymers are obtained [8].
- By thermal-oxidation of tetraethoxysilane superfine silicon dioxide (white soot) is obtained, it is used as a filler material.

Conclusions

1. Design works on the small-scale pilot plant for PSF with productivity 400 kg / year are completed. Works on creation and testing of the small-scale pilot plant can be executed within 25 months. Also, the initial data on design of the industrial scale plant with productivity above 100 tones per year and estimated project cost for stages will be developed.

2. At creation of industrial scale production the specific energy consumption and cost of production will be reduced in 10 times because of:

- thermal energy recuperation;
- increases of productivity of units and devices:
- converting of all technological stages into continuous process mode;
- decrease of specific number of workers.

Table 3. Characteristics of commodities produced

Name	Parameters of quality
Main production	
PSF	Specific electric resistance of monocrystal, Ω·cm – not less than 10000. Lifetime of non-uniform carriers, μs, more than 1000
Monosilane	Mass share of elements, %, not more than: B – $6x10^{-5}$; Fe - $1x10^{-4}$; Ni - $5x10^{-5}$; Mn - $1x10^{-6}$; Al - $5x10^{-5}$; Cu - $1x10^{-4}$; Mg - $5x10^{-5}$. volume share of oxygen-containing organic admixtures, %, not more than $1x10^{-3}$
By-product	
Silicasol-30	Content of silicon dioxide (SiO_2), %mass – 30. pH of the solution– 7,5 – 9,0. kinematic viscosity at 20^0C, cst – not more than 20. Density at 20^0C, kg/m^3 – 1200 – 1210.
Triethoxysilane	Main product content, %mass – 99,87. Micro admixtures content, %mass - B – $3x10^{-7}$; Fe - $5x10^{-6}$; Ti - $1x10^{-6}$; Mn - $1x10^{-6}$; Al - $1x10^{-6}$; Cu - $1x10^{-7}$; Mg - $1x10^{-7}$; Ca - $5x10^{-6}$; Cr - $5x10^{-6}$.
Tetraethoxysilane	Main product content, %mass – 99,8 Micro admixtures content, %mass - B – $1x10^{-7}$; (Ti, Cu, V, Mo, Mn) - $5x10^{-7}$; (P, Zn, Pb, Sb, Cr, Co, As, Sn, Bi) - $1x10^{-6}$; Mg - $2x10^{-6}$; (Ca, Fe, Al) - $5x10^{-6}$; (Ta, Li, Cd) - $5x10^{-6}$.

Capital expenses will be simultaneously reduced due to:

- decrease of specific cost of the equipment, instrumentations, armatures, and pipelines;
- decrease of specific cost of civil and installation works

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Due to the development of the solar energy industry, a significant increase of polysilicon feedstock (PSF) production will be required in near future. The creation of special technology of solar grade polysilicon feedstock production is an important problem. Today, semiconductor-grade polysilicon is mainly manufactured using the trichlorosilane (SiHCl3) distillation and reduction. The feed-stock for trichlorosilane is metallurgical-grade silicon, the product of reduction of natural quartzite (silica). This polysilicon production method is characterised by high energy consumption and large amounts of wastes, containing environmentally harmful chlorine based compounds. In the former USSR the principles of industrial method for production of monosilane and polycrystalline silicon by thermal decomposition of monosilane were founded. This technology was proved in industrial scale at production of gaseous monosilane and PSF. We offered new chlorine free technology (CFT). Originality and novelty of the process were confirmed by Russian and US patents.

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